PESTICIDES

What are they?

Pesticides are a broad class of substances designed to kill, repel or otherwise disrupt living things that are considered pests. They include insecticides, herbicides, fungicides and anti-microbials, among other types of biocides. Normal field applications, spills, misuse or improper storage and disposal can all lead to pesticide contamination in groundwater. As pesticides breakdown in soil and groundwater or are absorbed and metabolized by the target pest, some are converted into related compounds called metabolites, which may also be harmful to the pest or other living things.

Pesticide application sign. Photo: DATCP.

The health effects of exposure to pesticides or pesticide metabolites vary by substance. About 30 pesticides (and some pesticide metabolites) currently have ~~a~~ ch. NR 140 groundwater quality standards (WI NR 140.10), and a smaller number have an established maximum contaminant level (MCL), applicable at public drinking water systems (WI NR 809.20). However, at least 90 different pesticides are used on major crops in Wisconsin (WASS, 2006). Occasionally, pesticides and pesticide metabolites that do not have a NR 140 groundwater quality enforcement standard (ES) or public drinking water MCL are detected in drinking water supplies, and information on the health effects of these pesticide compounds is often very limited or difficult to evaluate. It is also difficult to predict the health effects of multiple pesticides in drinking water; several studies have indicated that pesticide mixtures can have different health effects than exposure to individual pesticides at the same concentrations (Porter, 1999; Hayes et al., 2006).

Periodically the Department of Agriculture, Trade and Consumer Protection (DATCP) identifies pesticides that are newly approved, have a high rate of use, or have been detected ("parent" compound or metabolites) in groundwater. These pesticides may be candidates for state groundwater standards development. Identified candidate pesticides and metabolites may be included on a list of substances that the DNR transmits to the WI Department of Health Services (DHS) requesting that DHS review available toxicologic information and, if appropriate, provide recommendations for ch. NR 140 groundwater quality standards.

In March 2018 and April 2019, lists of substances designated "Cycle 10" and "Cycle 11", that included pesticides and pesticide metabolites, were sent to DHS for review. The pesticides and metabolites on the Cycle 10 list included eight herbicides and herbicide metabolites: Isoxaflutole, Isoxaflutole DKN, Isoxaflutole BA, Glyphosate,

Glyphosate AMPA, Thiencarbazone-methyl, Sulfentrazone and Dacthal TPA & MTP degradates, and three neonicotinoid insecticides: Thiamethoxam, Imidacloprid and Clothianidin. The Cycle 11 list included five herbicides: Metalaxyl, Flumetsulam, Fomesafen, Hexazinone, Saflufenacil, and one insecticide, Chlorantraniliprole. DNR received recommendations from DHS on all 16 pesticide/pesticide metabolite standards (see https://www.dhs.wisconsin.gov/water/gws.htm).

Commonly detected pesticides and their metabolites which have established groundwater quality or drinking water standards in Wisconsin include atrazine, alachlor, metolachlor, and acetochlor.

Atrazine is an herbicide commonly used on corn. The groundwater quality ES for atrazine and its three chlorinated metabolites is 3 parts per billion (ppb). The drinking water MCL for atrazine (does not include metabolites) is 3 ppb. A number of epidemiological and animal studies have been conducted evaluating the potential health and environmental impacts from atrazine exposure (Hayes et al., 2002; ATSDR, 2003; Hayes et al., 2003; Hayes et al., 2006; Hayes et al., 2011; Craigin et al., 2011; Agopian et al., 2012; Agopian et al., 2013). People who drink water containing atrazine in excess of health-based standards over many years could experience problems with their cardiovascular system or reproductive difficulties.

Alachlor is an herbicide used on corn and soybeans. Use of alachlor in Wisconsin has been replaced by other herbicides in the same family (e.g., metolachlor, acetochlor) (NASS, 2015 and 2016), however, its metabolites still linger in groundwater. Both the groundwater quality enforcement standard (ES) and public drinking water MCL for alachlor are 2 parts per billion (ppb), and the groundwater quality ES for one of its metabolites, *alachlor ESA*, is 20 ppb. People who drink water containing alachlor in excess of health-based standards over many years could have problems with their eyes, liver, kidneys or spleen, or experience anemia, and may have an increased risk of getting cancer.

Metolachlor is an herbicide used widely on corn and soybeans, and on vegetable crops including peas, snap beans and potatoes. Both the parent and metabolite forms (metolachlor, metolachlor-ESA and metolachlor-OXA) are routinely detected in groundwater and health-based groundwater quality standards have been established for these compounds. The groundwater quality ES for metolachlor is 100 ppb, and the groundwater quality ES for metolachlor-ESA and OXA combined is 1,300 ppb. Although metolachlor and its metabolites are commonly detected in groundwater, the concentrations detected are typically well below their respective ESs.

Acetochlor is an herbicide used for pre-emergent control of weeds in corn. The state groundwater quality ES for acetochlor is 7 ppb. A groundwater quality ES of 230 ppb has also been established for the combined acetochlor metabolites, acetochlor ESA and acetochlor OXA. No public water supply MCL has been established for acetochlor or its metabolites. Animal studies have shown that oral exposure to acetochlor can

produce significant neurological effects (EPA, 2006). Acetochlor has been classified by the EPA as a "suggestive human carcinogen".

Occurrence in Wisconsin

In Wisconsin, the main source of pesticides in groundwater is agricultural herbicide and insecticide applications. For this reason, detection is more common in highly cultivated areas where agriculture is well established, notably in the south central, central and west-central parts of the state.

In 2016, DATCP conducted a statewide statistical survey of agricultural chemicals in groundwater that found an estimated 41.7% of private wells in Wisconsin contained a pesticide or pesticide metabolite (DATCP, 2017), up from 33% of private wells in a similar survey conducted in 2007 (DATCP, 2008). The primary metabolites of metolachlor and alachlor, metolachlor ESA and alachlor ESA, were the two most commonly detected pesticide products in those surveys. Atrazine and its metabolites, known collectively as the total chlorinated residues of atrazine (atrazine TCR), were also prevalent and occurred in about 23% of wells. Less than 1% of well samples with atrazine TCR detections had atrazine TCR levels that exceeded the groundwater quality ES of 3 ppb.

GCC Agency Actions

Serious concerns about pesticide contamination in Wisconsin were first raised in 1980 when aldicarb, a pesticide used on potatoes, was detected in groundwater near Stevens Point. The DNR, DATCP and other agencies responded to concerns by implementing monitoring programs and conducting groundwater surveys, initially testing exclusively for aldicarb, (Rothschild et al., 1982; Kraft 1990), but soon expanding to other pesticides and pesticide metabolites (Postle and Brey, 1988). DATCP also developed rules to restrict aldicarb use in areas vulnerable to groundwater contamination.

A plane sprays pesticides on a field. Photo: DATCP.

When findings from these sampling surveys in the late 1980s and early 1990s showed that atrazine, a popular corn herbicide, was particularly prevalent in groundwater across the state (LeMasters and Doyle, 1989; Cowell and LeMasters, 1992), special projects were conducted to investigate how and why it reaches groundwater. Notably, researchers funded by the Wisconsin Groundwater Research and Monitoring Program (WGRMP) discovered that normal field application of atrazine – not just point spills and misuse – was an important source of atrazine in

groundwater (Chesters et al., 1990; Chesters et al. 1991). This knowledge, combined with other findings regarding the roles of soil, geology and agricultural management (Daniel and Wietersen, 1989; Lowery and McSweeney, 1992; Levy and Chesters 1995; Levy et al. 1998), allowed DNR and DATCP to effectively and fairly design both groundwater standards and the atrazine rule, as detailed in this profile on the experience.

Where atrazine use has been prohibited by the atrazine rule, follow-up studies demonstrate there is a clear reduction in atrazine levels, which generally drop below the groundwater standard in 2 to 7 years (DATCP, 2010). Many farmers would like the option to use atrazine in these areas, but they have adapted well to growing corn without it. A 2010 DATCP survey found that the vast majority of farmers in atrazine prohibition areas have not observed a decrease in yield, and that most believe it is not more difficult to control weeds with other alternatives. The survey found that there is an even split in those who think weed control is more vs. less costly without atrazine (DATCP, 2011a). By far, the most popular alternatives to atrazine are glyphosate-containing products such as Roundup. From a groundwater perspective, this is fortunate since glyphosate binds very tightly to soil and thus is generally not considered a groundwater threat. There are concerns, however, that overuse of glyphosate may lead to glyphosate-resistant weeds.

Many sampling programs initiated by DATCP, the DNR and other agencies in the mid-1980s to early 1990s are still ongoing today. The longest running sampling program for pesticides began in 1985 and is designed to evaluate the potential impact of agriculture on groundwater quality by sampling monitoring wells near selected agricultural fields in areas with high groundwater contamination potential. Testing in this program confirms that the metabolites of metolachlor and alachlor are the two most common pesticides products detected in groundwater near the monitoring well sites.

A DATCP review of data from samples it collected statewide from 2008 through 2016 revealed an increased occurrence of detections of neonicotinoid insecticides in samples collected from monitoring wells, irrigation wells, private wells, and surface water samples. DATCP reported detections of the neonicotinoid insecticides clothianidin, imidacloprid and thiamethoxam in samples from monitoring wells, irrigation wells, and private wells tested, with most detections occurring in sandy irrigated vegetable growing areas in the Central Sands region and on terraces of the Wisconsin River Valley (DATCP, 2019). The review also reported that out of 34 streams sampled statewide, multiple

Preparing to sample monitoring wells near an agricultural field. Photo: DATCP.

detections of imidacloprid and thiamethoxam were reported year-round in two streams also located within the Central Sands region. Concentrations of total neonicotinoids detected in these streams pose significant concerns for aquatic invertebrates and other non-target aquatic species present in the streams. The report detailing the findings of DATCP's review was shared with U.S. EPA as they continue to evaluate the role that these compounds may have in declining pollinator populations nationwide.

Another study that has been repeated annually since 1995 focuses on re-sampling wells that once previously exceeded a pesticide standard. Over 160 wells have been sampled multiple times in this program, and over time, atrazine levels have been shown to decline in about 80% of the wells (DATCP, 2010). Many of these wells are located in what are now atrazine prohibition areas and the declines are likely the direct result of restrictions placed on the use of this pesticide in these areas.

DATCP has also conducted a statewide, statistically designed survey of agricultural chemicals in Wisconsin groundwater five times since the early 1990s (1994, 1996, 2001, 2007 and 2016). In 2016, nearly four hundred samples from private drinking water wells were analyzed for 101 pesticide compounds, including 70 herbicides, 26 insecticides, 4 fungicides and 1 pesticide safener. Health standards have been established for 27 of the compounds analyzed. In addition to capturing the current picture of agricultural chemicals in groundwater, this series of studies relates these findings to land use and compares results of the 2016 survey to those of previous surveys. The final report of the results of the 2016 survey was published in early 2017 (DATCP 2017). DATCP is planning the next survey for 2023. Publications of DATCP surveys are available on the web at:
https://datcp.wi.gov/Pages/Programs_Services/GroundwaterReports.aspx

Future Work

DATCP began oversight of a Stipulated Agreement and Special Order between DATCP and Bayer CropScience (BCS) related to the limited use of the BCS pesticide isoxaflutole in Wisconsin. Isoxaflutole is a relatively new corn herbicide that has a high likelihood of leaching to groundwater. The agreement allows for use on corn grown in just 12 counties (Columbia, Dane, Dodge, Fond du Lac, Grant, Green, Jefferson, Lafayette, Rock, Sauk, Walworth and Waukesha) while BCS performs specific studies over five years that are intended to clarify the potential for surface or groundwater impacts. Throughout the study, BCS will monitor surface water and tile drainage sites that receive isoxaflutole applications. They will also monitor groundwater at eight groundwater monitoring sites that receive three applications of the pesticide over the multi-year study period.

Further development of health standards and laboratory methods is of paramount importance for keeping pace with the evolving use of agricultural chemicals to ensure that the agricultural success that is so crucial for our state is fairly balanced with the protection of groundwater and human health.

Update on Groundwater Standards for Pesticides

As part of a continuing commitment to protect public health, public welfare, and the environment, the DNR periodically updates groundwater quality standards in ch. NR 140, Wis. Adm. Code. In March 2018 and April 2019, lists of substances designated "Cycle 10" and "Cycle 11", that included pesticides and pesticide metabolites, were sent to DHS for review. The pesticides and metabolites on the Cycle 10 list included eight herbicides and herbicide metabolites: Isoxaflutole, Isoxaflutole DKN, Isoxaflutole BA, Glyphosate, Glyphosate AMPA, Thiencarbazone-methyl, Sulfentrazone and Dacthal TPA & MTP degradates, and three neonicotinoid insecticides: Thiamethoxam, Imidacloprid and Clothianidin. The Cycle 11 list included five herbicides: Metalaxyl, Flumetsulam, Fomesafen, Hexazinone, Saflufenacil, and one insecticide, Chlorantraniliprole.

DNR received recommendations from DHS on all 16 pesticide/pesticide metabolite groundwater quality standards (see https://www.dhs.wisconsin.gov/water/gws.htm) and began rulemaking to incorporate the DHS recommendations into ch. NR 140. On February 23, 2022, the DNR Natural Resources Board (NRB) considered approval of proposed revisions to ch. NR 140 to incorporate the DHS Cycle 10 groundwater standard recommendations, including recommended standards for pesticides and pesticide metabolites, into ch. NR 140. The NRB did not approve the proposed NR 140 Cycle 10 groundwater quality standards at their Feb. 23, 2022 meeting. The DNR has currently placed rulemaking, to incorporate the DHS Cycle 11 groundwater standard recommendations into ch. NR 140, on hold.

Further Reading

DHS resources for contaminants in drinking water
DNR overview of pesticides in drinking water wells
DATCP water quality reports
DATCP Home Groundwater Standards for Pesticides (wi.gov)

References

Agopian, A. J. et al. 2012. Maternal residential atrazine exposure and risk for choanal atresia and stenosis in offspring. Journal of Pediatrics, 162(3):581-586. Available at https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4105141/

Agopian, A. J. et al. 2013. Case-control study of maternal residential atrazine exposure and male genital malformations. American Journal of Pediatrics, 161(5):977-982.

ATSDR. 2003. Toxicological Profile for Atrazine. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry. Available at http://digicoll.library.wisc.edu/cgi-bin/EcoNatRes/EcoNatRes-idx?id=EcoNatRes.ChestersSources

Chesters, G., G. V. Simsiman, R. N. Fathulla, B. J. Alhajjar, R. F. Harris, J. M. Harkin, J. Levy. 1990. Degradation of atrazine, alachlor, metolachlor in soils and aquifer materials. Wisconsin groundwater management practice monitoring project, DNR-047. Available at http://digicoll.library.wisc.edu/cgi-bin/EcoNatRes/EcoNatRes-idx?id=EcoNatRes.ChestersDegradation

Chesters, G., J. Levy, D. P. Gustafson, H. W. Read, G. V. Simsiman, D. C. Liposcak, Y. Xiang. Sources and extent of atrazine contamination of groundwater at Grade A dairy farms in Dane County, WI. Wisconsin groundwater management practice monitoring

project, DNR-065. Available at http://digicoll.library.wisc.edu/cgi-bin/EcoNatRes/EcoNatRes-idx?id=EcoNatRes.ChestersSources

Cowell, S. E. and LeMasters G. S. 1992. Follow up to the grade A dairy farm well water quality survey. Wisconsin groundwater management practice monitoring project, DNR-070. Available at http://digicoll.library.wisc.edu/cgi-bin/EcoNatRes/EcoNatRes-idx?id=EcoNatRes.CowellFollow

Cragin, L. A. et al. 2011. Menstrual cycle characteristics and reproductive hormone levels in women exposed to atrazine in drinking water. Environmental Research, 111(8):1293-301.

Daniel, T. and R. Wietersen. 1989. Effect of soil type on atrazine and alachlor movement through the unsaturated zone. Wisconsin groundwater management practice monitoring project, DNR-062. Available at http://digicoll.library.wisc.edu/cgi-bin/EcoNatRes/EcoNatRes-idx?id=EcoNatRes.DanielEffect

DATCP, 2008. Groundwater Quality: Agricultural Chemicals in Wisconsin Groundwater. Wisconsin Department of Agriculture, Trade and Consumer Protection, Environmental Quality Section, ARM Pub 180. 22 pp. Available via email request at datcppublicrecords@wi.gov or at https://datcp.wi.gov/Pages/Programs_Services/GroundwaterReports.aspx

DATCP, 2010. Fifteen years of the DATCP exceedance well survey. Wisconsin Department of Agriculture, Trade and Consumer Protection. Available via email request at datcppublicrecords@wi.gov

DATCP. 2011a. Final report on the 2010 Survey of Weed Management Practices in Wisconsin's Atrazine Prohibition Areas. Wisconsin Department of Agriculture, Trade and Consumer Protection, ARM Pub 215. Available via email request at datcppublicrecords@wi.gov

DATCP, 2017. Wisconsin Groundwater Quality: Agricultural Chemicals in Wisconsin Groundwater. Wisconsin Department of Agriculture, Trade and Consumer Protection, Environmental Quality Section, ARM Pub 264. 26 pp. Available via email request at datcppublicrecords@wi.gov or at https://datcp.wi.gov/Pages/Programs_Services/GroundwaterReports.aspx

DATCP, 2019. Neonicotinoid Pesticides in Wisconsin Groundwater and Surface Water. Wisconsin Department of Agriculture, Trade and Consumer Protection, Environmental Quality Unit, ARM Pub
315. 49 pp. Available via email request at datcppublicrecords@wi.gov or at https://datcp.wi.gov/Pages/Programs_Services/GroundwaterReports.aspx

EPA, 1995. Reregistration Eligibility Decision (RED) Metolachlor. EPA 738-R-95-006. April 1995. Available at https://archive.epa.gov/pesticides/reregistration/web/pdf/0001.pdf

EPA, 2006. Acetochlor. Revised HED Chapter of the Tolerance Reassessment Eligibility Decision (TRED) Document. March 2006.

Hayes, T., K. Hason, M. Tsui, A. Hoang, C. Haeffele, A. Vonk. 2002. Feminization of male frogs in the wild. Nature, 419:895-896.

Hayes, T., K. Hason, M. Tsui, A. Hoang, C. Haeffele, A. Vonk. 2003. Atrazine-induced hermaphroditism at 0.1 PPB in American Leopard Frogs (Rana pipiens): laboratory and

field evidence. Environmental Health Perspectives, 111:568-575. Available at https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1241446/

Hayes, T. B., et al. 2006. Pesticide mixtures, endocrine disruption, and amphibian declines: are we underestimating the impact? Environmental Health Perspectives, 114(suppl 1):40-50. Available at https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1874187/

Hayes, T. B., et al. 2011. Demasculinization and feminization of male gonads by atrazine: Consistent effects across vertebrate classes. The Journal of Steroid Biochemistry and Molecular Biology, 127(1- 2):64-73. Available at https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4303243/

Kraft, G. 1990. Fate of aldicarb residues in a groundwater basin near Plover, Wisconsin. Ph.D. dissertation, Department of Soil Science, UW-Madison.

LeMasters, G. S. and D. J. Doyle. 1989. Grade A dairy farm well water quality survey. Wisconsin groundwater management practice monitoring project, DNR-052. Available at http://digicoll.library.wisc.edu/cgi-bin/EcoNatRes/EcoNatRes-idx?id=EcoNatRes.LeMastersGrade

Levy, J. and G. Chesters. 1995. Simulation of atrazine and metabolite transport and fate in a sandy-till aquifer. Journal of Contaminant Hydrology 20(1-2):67-88.

Levy, J., G. Chesters, D. P. Gustafson, H. W. Read. 1998. Assessing aquifer susceptibility to and severity of atrazine contamination at a field site in south-central Wisconsin, USA. Hydrogeology Journal, 6(4):483- 499.

Lowery, B. and K. McSweeney. 1992. Effect of soil type, selected best management practices, and tillage on atrazine and alachlor movement through the unsaturated zone. Wisconsin groundwater management practice monitoring project, DNR-066. Available at http://digicoll.library.wisc.edu/cgi-bin/EcoNatRes/EcoNatRes-idx?id=EcoNatRes.LoweryEffect

NASS. 2015. Wisconsin Agricultural Chemical Use, Corn and Potatoes, Fall 2014. United States Department of Agriculture, National Agricultural Statistics Service. Available at

NASS. 2016. Wisconsin Agricultural Chemical Use, Soybeans, Fall 2015. United States Department of Agriculture, National Agricultural Statistics Service.

Porter, W.P., et al. 1999. Endocrine, immune and behavioral effects of aldicarb (carbamate), atrazine (triazine) and nitrate (fertilizer) mixtures at groundwater concentrations. Toxicology and Industrial Health 15(1-2): 133-150.

Postle, J. K. and Brey K. M. 1988. Results of the WDATCP groundwater monitoring for pesticides. Wisconsin groundwater management practice monitoring project, DNR-002. Available at http://digicoll.library.wisc.edu/cgi-bin/EcoNatRes/EcoNatRes-idx?id=EcoNatRes.PostleResults

Rothschild, E. R., R. J. Manser, M. P. Anderson. 1982. Investigation of aldicarb in ground water in selected areas of the Central Sand Plain of Wisconsin. Ground Water 20(4):437-445.

WASS. 2006. Wisconsin Pesticide Use. Wisconsin Department of Agriculture, Trade and Consumer Protection. United States Department of Agriculture, National Agricultural Statistics Service.